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X-RAY ANALYSIS OF FROZEN STYRENE AT −180°C

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(*Received for publication, January 15, 1958*)

Plate IV

ABSTRACT Debye-Scherrer pattern of pure monomeric styrene frozen and cooled to −180°C has been studied. Analysis of the pattern shows that the crystals might belong to C^1_{2v} space group assuming the molecule to possess a plane of symmetry or to Q^1_h space group, in case there is no symmetry in the molecule. The dimensions of the unit cell are found to be a = 9.90Å, b = 8.89 Å and c = 7.84 Å. The number of molecules in the unit cell as determined from the measured density of the crystals is found to be four.

Similar pattern of polystyrene at 30°C shows four diffuse halos corresponding to the spacings of 7.51 Å, 3.49 Å, 2.39 Å and 1.95 Å, of which the first is the most intense one.

INTRODUCTION

From the results of the investigation on the Raman spectra of styrene and its polymer at −180°C it was concluded (Roy, 1954) that the low-frequency Raman lines observed in the case of monomer at −180°C might be due to the translational oscillation of the benzene nuclei connected to each other through virtual bonds giving some regular arrangements in the surrounding molecules. In the case of the polymer a continuous wing accompanying the Rayleigh line upto 90 cm^{-1} was observed, and this was attributed to the irregular arrangement of the molecules. As shown by Whitby (1927), the polymer is amorphous. The frozen monomeric styrene appeared to be crystalline, but its structure was not known. The object of the present investigation was to determine the crystal structure of frozen monomeric styrene at −180°C, because such information might be helpful in understanding the origin of the low-frequency Raman lines. For this purpose the Debye-Scherrer patterns of monomeric styrene at −180°C have been photographed and the results of the analysis of the patterns have been discussed in the present paper. For comparison, the Debye-Scherrer pattern of poly-styrene at 30°C has also been studied in order to find out the predominant spacings shown by the halos.

EXPERIMENTAL

A sample of styrene (monomer) was carefully purified as described earlier (Roy, 1954) and was used to photograph the Debye-Scherrer patterns. The polymer prepared in the laboratory from pure monomeric styrene (Roy, 1954) was also used for studying the Debye-Scherrer pattern. A Seifert X-ray tube running at 32KV and 26 mA was used to photograph these patterns. The X-ray tube was provided with a copper target and a nickel filter was used to cut off the $K\beta$ radiation. An exposure of about 2 hours was required for recording each pattern.

The patterns at $-180°$C were photographed by the method described by Krishnamurti and Sen (1956), but the sample was rotated about a vertical axis intermittently. The radius of the camera was measured accurately by taking a Debye-Scherrer pattern of rock salt.

RESULTS AND DISCUSSION

The pattern due to monomeric styrene at $-180°$C is reproduced in figure 1, Plate IV, and that due to polymeric styrene at 30°C in figure 2, Plate IV.

The pattern due to monomeric styrene at $-180°$C shows a large number of rings, and therefore, the substance is crystalline at this temperature The values of $\sin^2\theta$ for the rings were calculated and these are given in the first column of Table I. The first three spacings were assumed to be those due to (100), (010) and (001) planes respectively, and following Lipson's (1949) method, the differences between $\sin^2\theta$ were plotted on a graph paper. It was observed that the differences 0.024, 0.030 and 0.010 are repeated several times. So the assignments were assumed to be correct and the following values of the constants were assumed to calculate the spacings of the planes on the assumption that the crystal belongs to the orthorhombic system :

$$\frac{\lambda^2}{4a^2} = 00604, \quad \frac{\lambda^2}{4b^2} = .00750, \quad \frac{\lambda^2}{4c^2} = .00964.$$

From these values of the constants we get, $a = 9.90$Å, $b = 8.89$Å, and $c = 7.84$ Å.

The density of the frozen monomer at $-180°$C was measured by a method previously described by Biswas and Sirkar (1957) and was found to be 1.012, taking the density of liquid styrene at 31°C to be 0.8966. This gives the number of molecules in the unit cell as 4.07 which may be taken as 4.

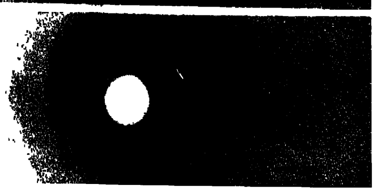
From a consideration of the results in Table I and the above value of the number of molecules per unit cell two possible space groups may be ascribed to the crystals of frozen monomeric styrene at $-180°C$. On the assumption of existence of a plane of symmetry in the monomeric styrene molecule, which is not unlikely from its molecular formula, and the number of asymmetric molecules required per unit cell to be 8, *i.e.*, double of the calculated value, the space group of the crystals may be C_{2v}^1. In case there is no symmetry in the molecules Q_h^1 space

Indian Journal of Physics, Vol XXXII, No. 3

PLATE IV

Fig 1

Fig 2



Debye-Scherrer patterns
Radius of the camera, 4·5 cms

Fig 1. Frozen monomeric styrene at −180°C
Fig 2 Polystyrene at 30°C

TABLE I

Radius of the Camera 4.50 cm.

Data for the Debye-Scherrer pattern of styrene at −180°C

$\sin^2\theta$ (observed)	$\sin^2\theta$ (calculated)	Difference	Spacings in Å	Proposed indices & intensities
.00604	.00604	.00000	9.90	100 (s)
.00750	.00750	.00000	8.89	010 (s)
.00964	.00964	.00000	7.84	001 (m)
.02402	.02416	.00014	4.97	200 (s)
.03054	.03000	.00054	4.40	020 (m)
.03187	.03166	.00021	4 31	210 (v.s)
.03651	.03604	.00047	4.03	120 (m)
.03860	.03856	.00004	3 92	002 (s)
.05253	05210	.00043	3.36	112 (w)
.05478	.05416 .05436	.00062 .00042	3.29	220 300 (m)
.06439	.06400	.00039	3.03	301 (m)
.06714	.06750	.00036	2.97	030 (m)
.08271	.08318	.00047	2.68	131 (w)
.08662	.08676	.00014	2.62	003 (m)
.10030	.10030	.00000	2.43	113 (m)
.1198	.1200	.0002	2.22	040 (m)
.1304	.1302	.0002	2.13	232 (m)
.1407	.1409	.0002	2.05	223 (m)
.1590	.1586	.0004	1.93	042 (m)
.1645	.1641	.0004	1 90	430 (s)
.2113	.2117	.0004	1 67	250 (w)
.2326	.2321	.0005	1.60	152 (s)

group can be ascribed to the crystals. It is not possible to decide from these data whether the molecule has a plane of symmetry in the crystal or not.

The Debye-Scherrer pattern of the polymer at 30°C shows one very intense halo and three comparatively weaker halos. The corresponding spacings are 7.51Å, 3.49 Å, 2.39 Å and 1.95 Å respectively. It is interesting to note that although these spacings are near to some spacings observed in the case of the frozen monomer the relative intensities are entirely different in the latter case. In the of case the polymer the spacing 7.51 Å is the most predominant one and this may correspond to the width of the molecule.

ACKNOWLEDGMENT

The author is indebted to Professor S. C Sirkar, D.Sc., F.N.I for his kind interest and constant guidance during the work.

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